

Neutron Scattering and Molecular Simulations: Synergistic Probes of Nanoscale Structure and Dynamics in Complex Polymer-based Materials

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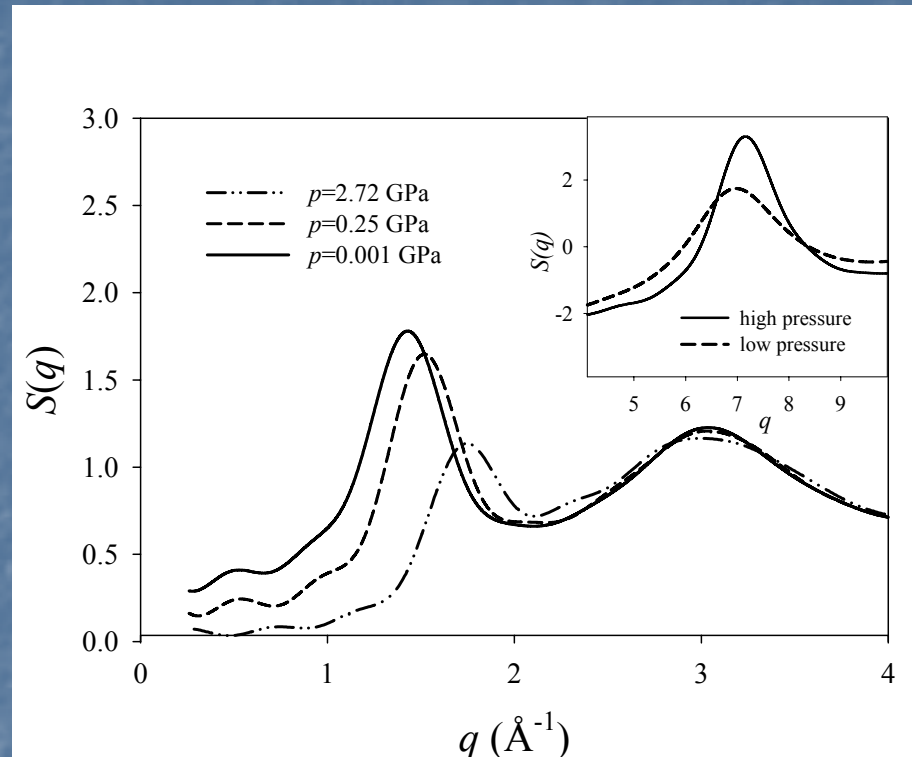
Outline

- Methods
- Examples of Synergism
 - polymer structure
 - polymer dynamics
- Polymer-nanoparticle Composites (PNPCs)
- Self-association of Polymer-grafted Nanoparticles
- Conclusions

Methods

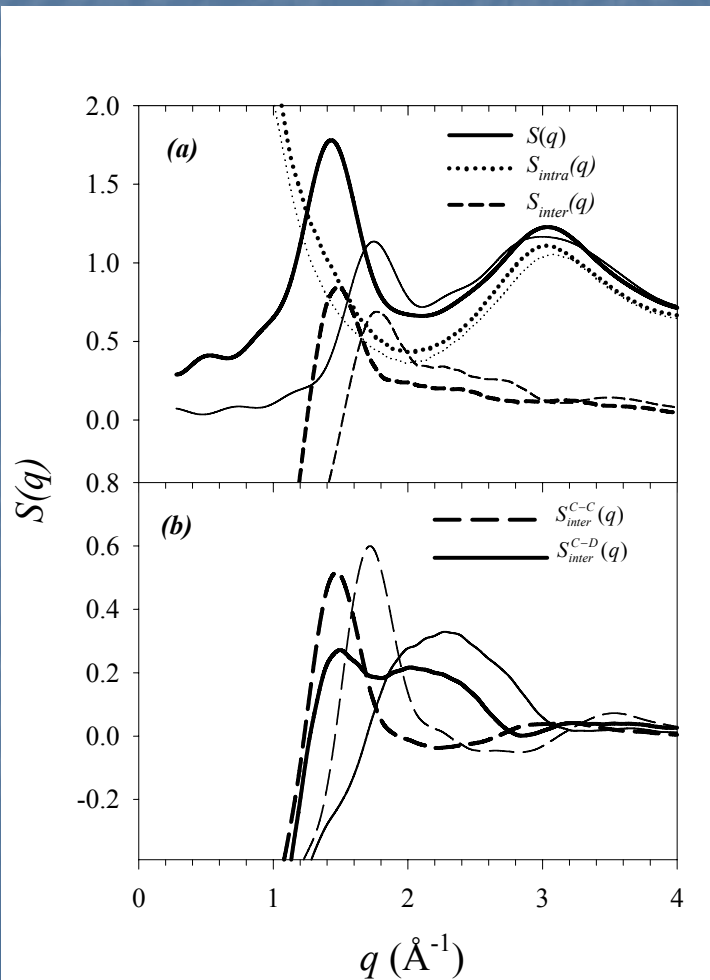
- Static neutron scattering to determine the static structure factor $S(q)$ with emphasis on nanometer-scale structure
- Dynamic neutron scattering to determine the coherent intermediate dynamic structure factor $S(q,t)$ (NSE) or the incoherent intermediate dynamic structure factor $I(q,t)$ (QENS/FT)
- Molecular dynamics simulations utilizing atomistic models with quantum-chemistry based potentials or multiscale simulations based upon atomistic simulations

Nanoscale Structure of 1,4-PBD Under High Pressure



➤ Recent neutron scattering studies of polymer melts have shown apparently anomalous behavior in the response of polymer melts to high pressure at the nanometer scale

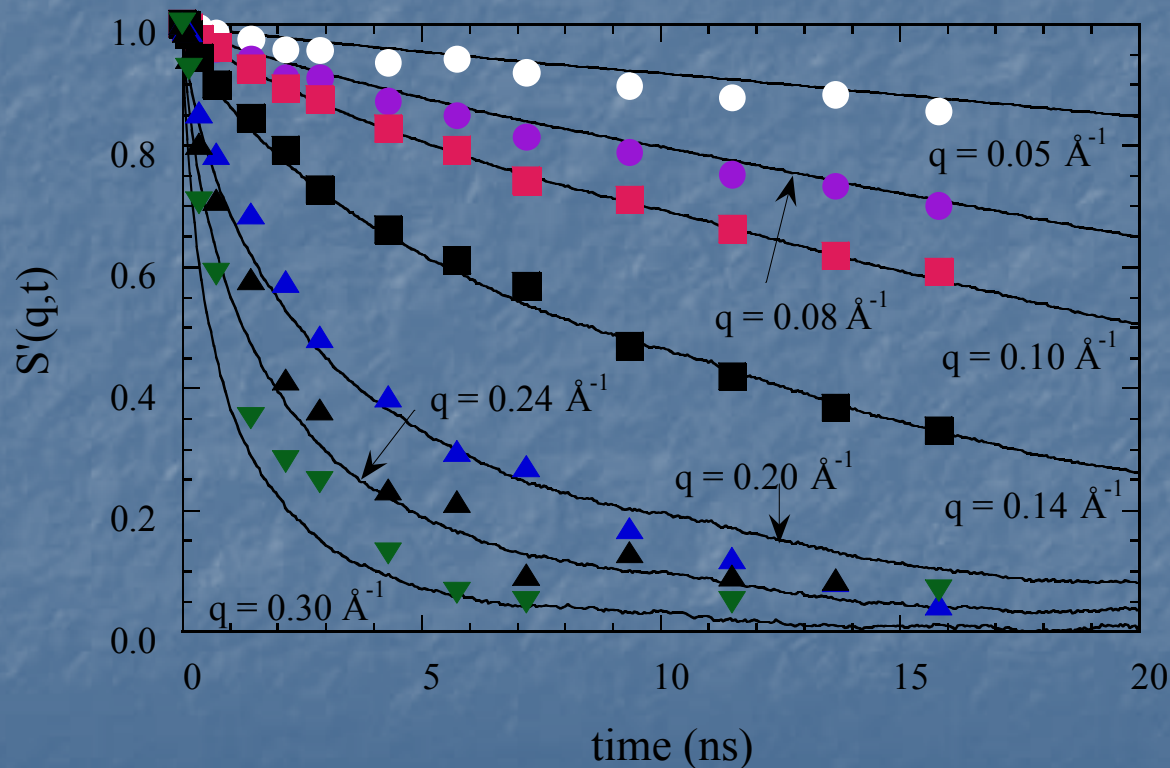
Nanoscale Structure of 1,4-PBD under High Pressure



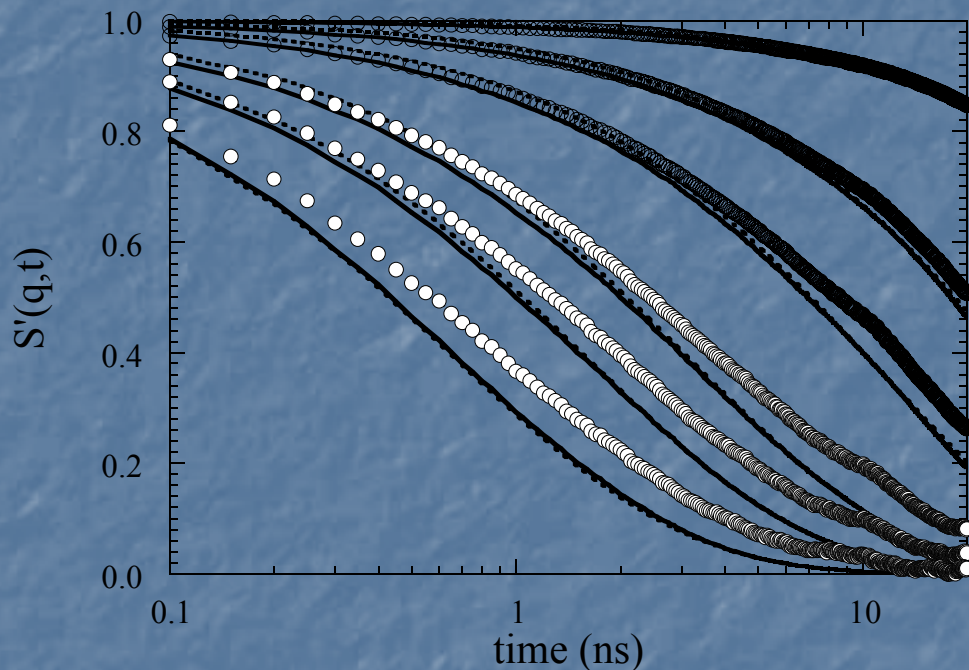
- Atomistic MD simulations reproduce experimental behavior
- Scattering from the polymer backbone exhibits the expected trends
- Simulations reveal that experimentally observed behavior can be associated with C-D correlations

Single-Chain Coherent Dynamic Structure Factor for PBD (353 K)

$$S'(q,t) = S(q,t)/S(q) = \frac{\sum_{(m,n)} \langle \sin[qR_{mn}(t)]/qR_{mn}(t) \rangle}{\sum_{(m,n)} \langle \sin[qR_{mn}(0)]/qR_{mn}(0) \rangle}$$



Single Chain Coherent Dynamic Structure Factor for PBD (353 K)



➤ Why does the Rouse model work so poorly?

- Chain stiffness
- Internal viscosity

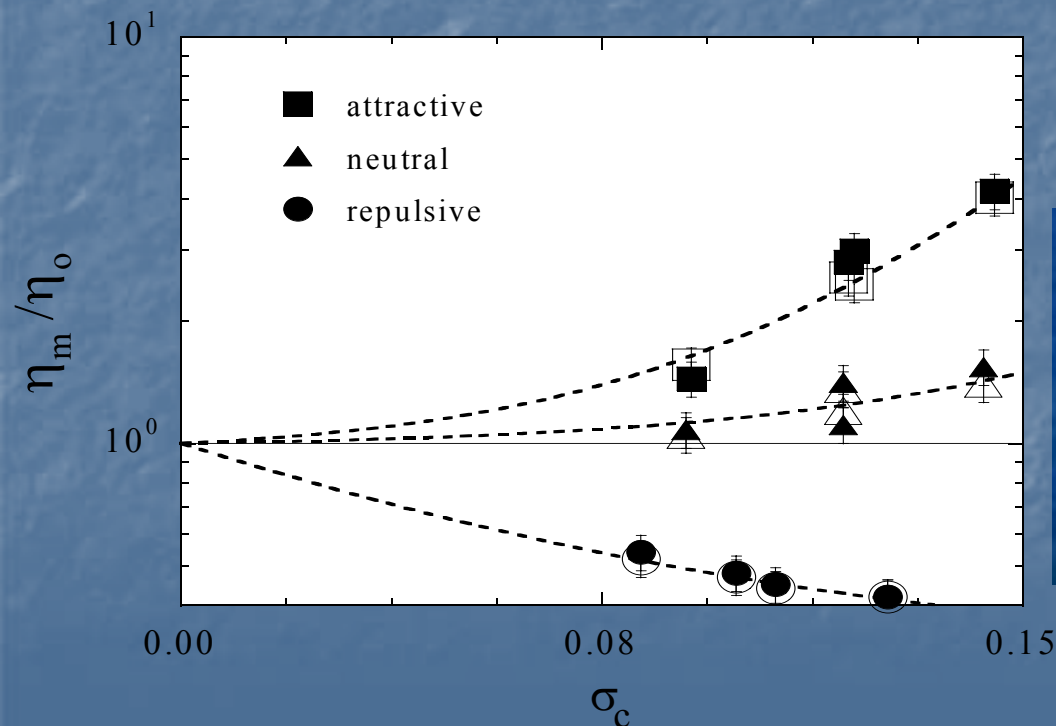
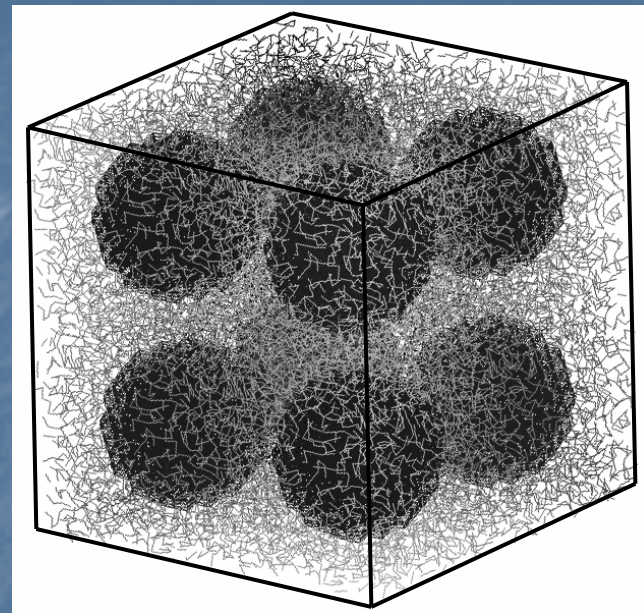
➤ Simulations reveal that the discrepancy in $S'(q,t)$ and Rouse predictions are the result of

- non-Gaussian distributed monomer displacements
- much of the non-Gaussian behavior results from intermolecular correlations



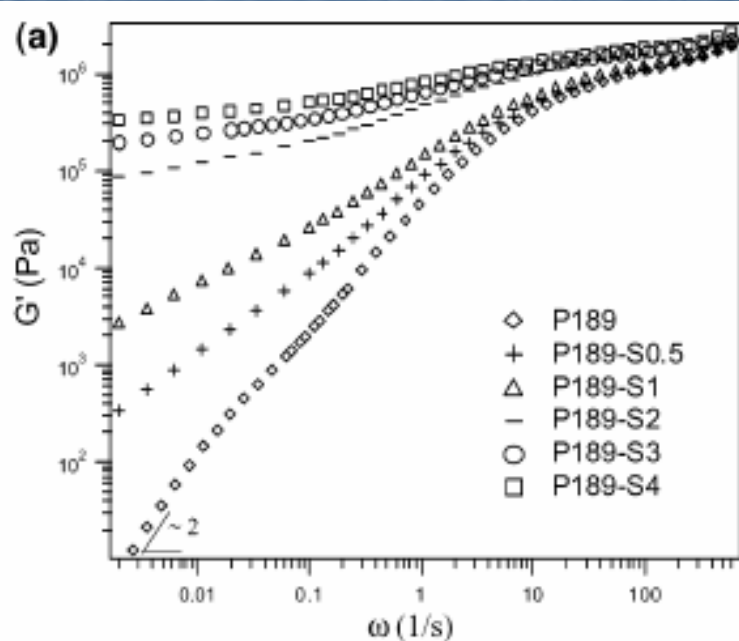
Polymer-nanoparticle Composites

- In order to efficiently design and fabricate PNPCs with desired properties, we must have the ability to predict their structure and response



- maximize interfacial area
- optimize structure
- “externally” control structure

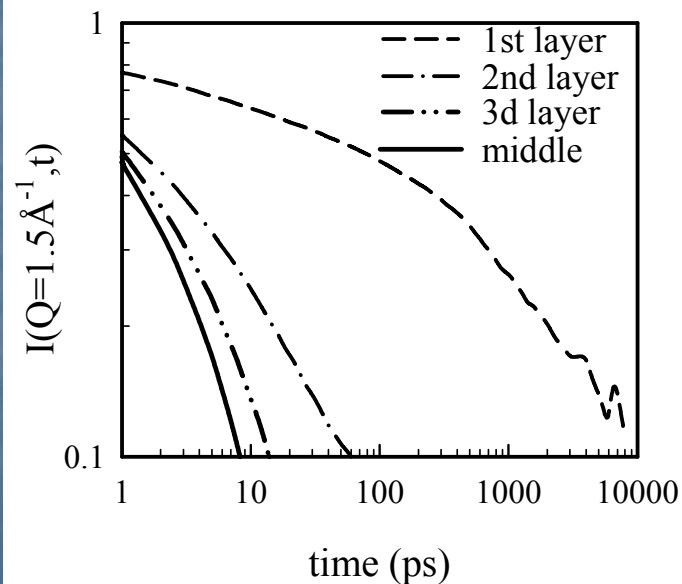
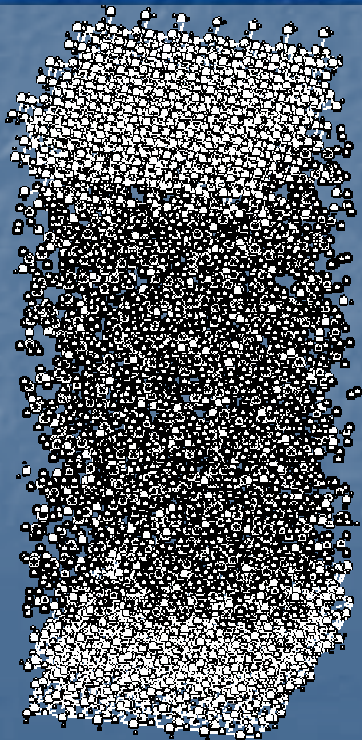
Polymer-nanoparticle Composites



- More dramatic influence on mechanical properties at low loading fractions have been seen experimentally
- The mechanism is unclear
 - Percolation of particles
 - Slowed polymer dynamics
 - Bridging of particles by the polymer
- QENS studies reveal slowing of polymer motion in PNPC's, but it is not dramatic

Polymer-nanoparticle Composites

- We have performed simulations studies of 10 chains of PEO ($M_w=2380$) sandwiched between TiO_2 surfaces of anatase crystal
- Overall slowing of polymer dynamics is consistent with QENS studies
- A dramatic slowing of polymer dynamics is seen for the first layer of polymer, i.e., polymer adsorbed to the surface

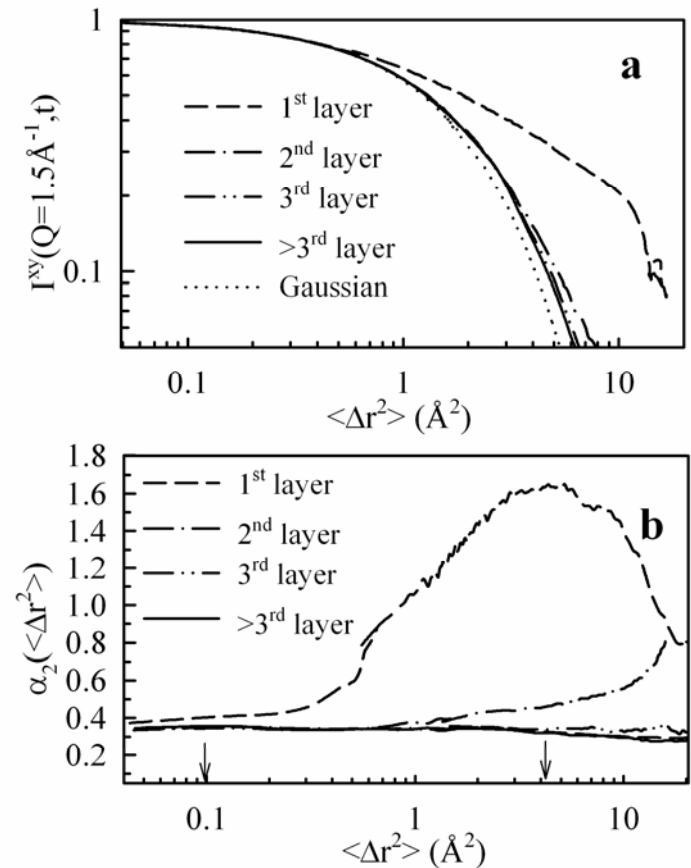


Polymer-nanoparticle Composites

➤ Slowing in the decay of $I(q,t)$ in for the first layer of polymer is due to

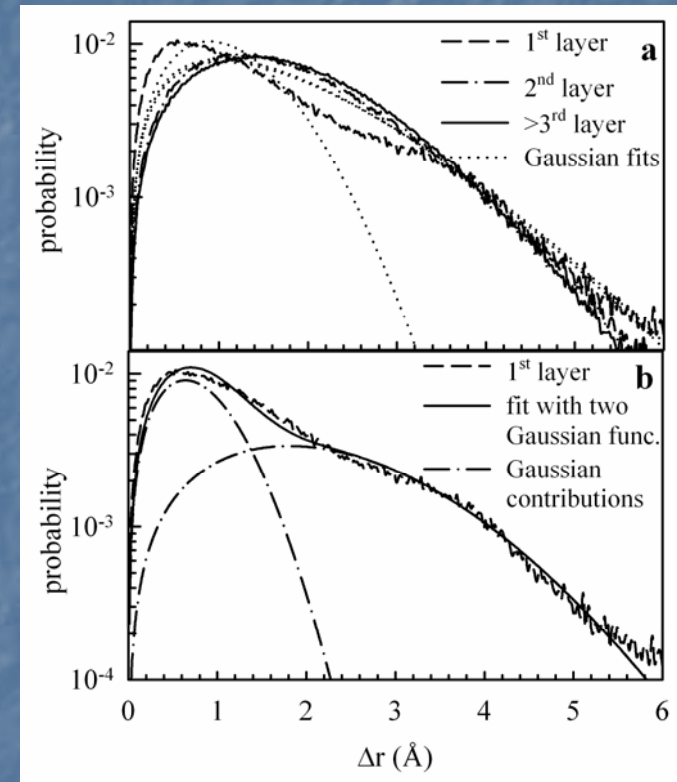
➤ Intrinsically slower motion

➤ Highly heterogeneous (non-Gaussian) motion along the surface)



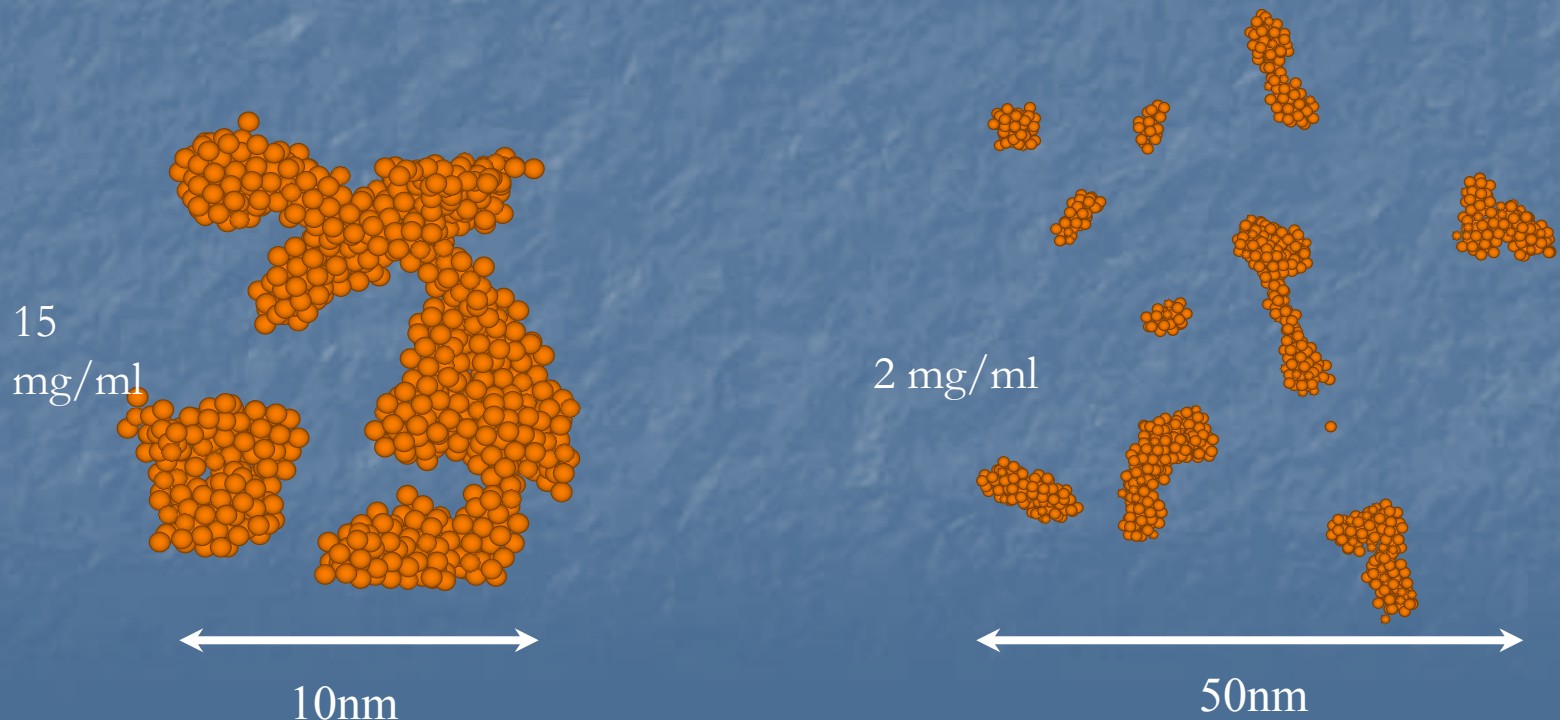
Polymer-nanoparticle Composites

- Both the intrinsic slowing and heterogeneity depend upon the strength of interaction between the surface and polymer and the structure of the surface
- Heterogeneity largely reflects motion along the surface induced by the structure of the surface

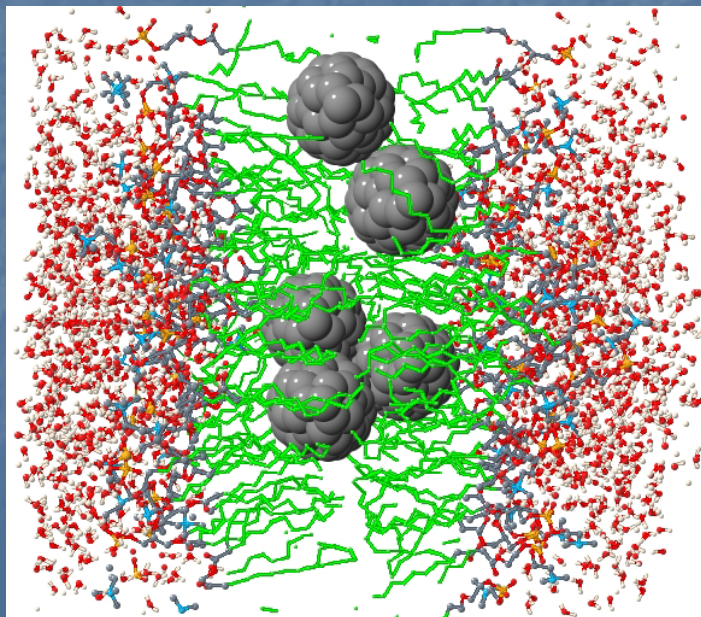
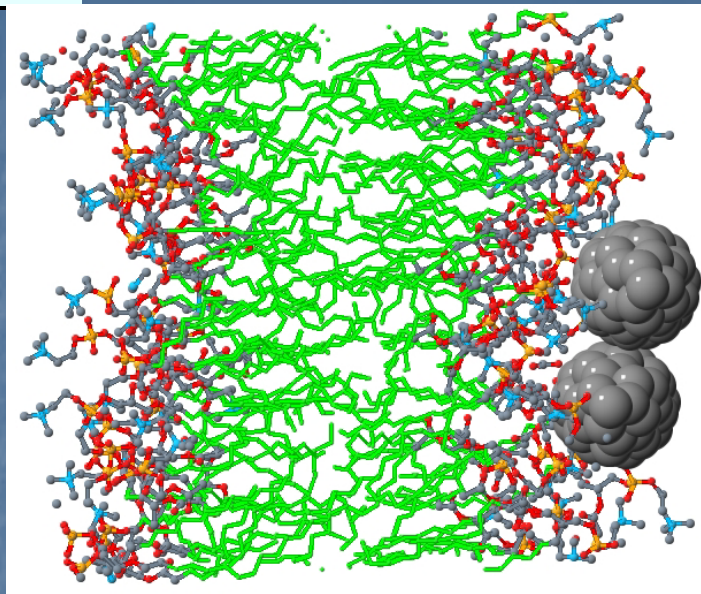
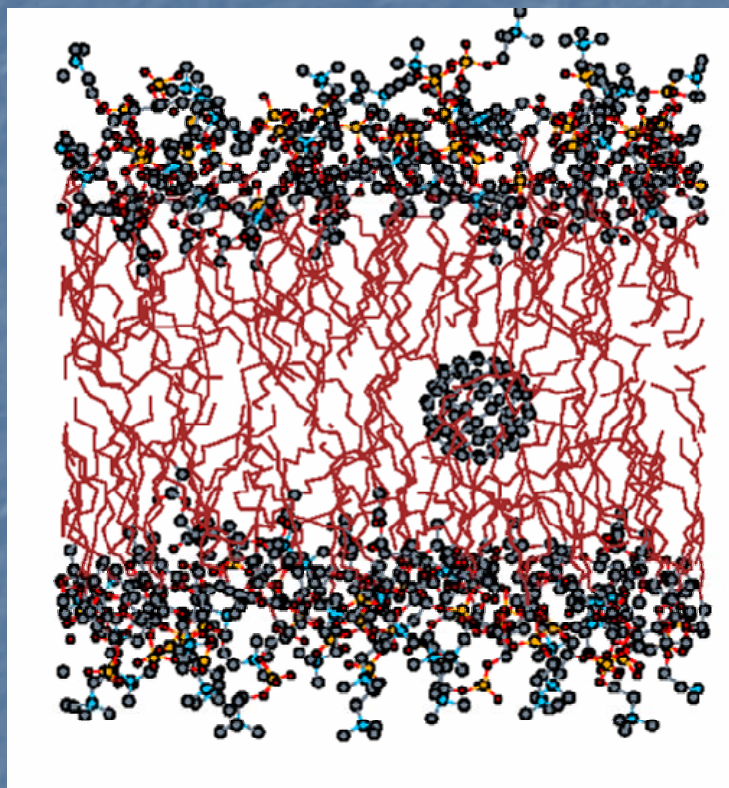


Nanoparticle Self-association

- Interpretation of static and dynamic structure factors in nanomaterials is complex because of the multiplicity of correlations that can be present on the nanometer length scale
- This is illustrated clearly in efforts to understand the aggregation of C_{60} fullerenes in aqueous solution: Time dependent, model independent

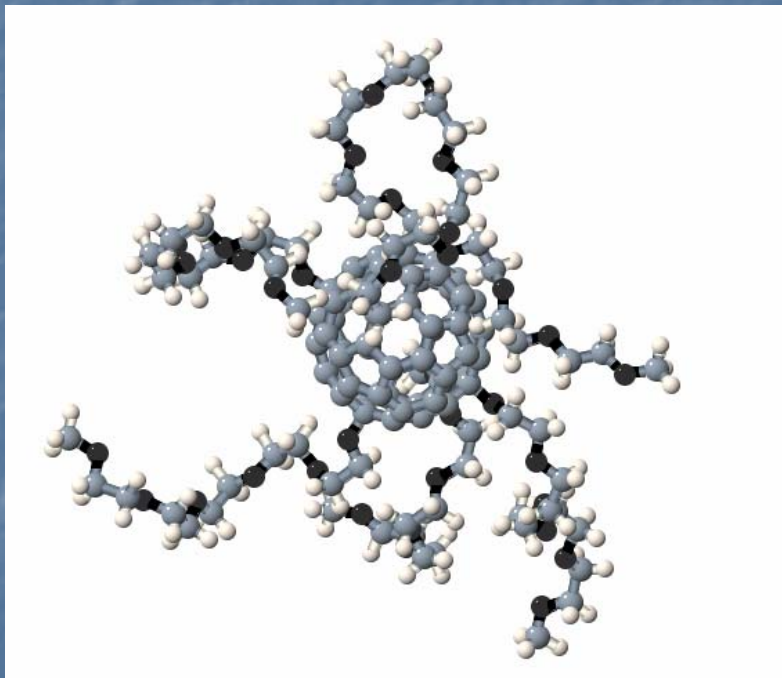


Nanoparticle Self-association

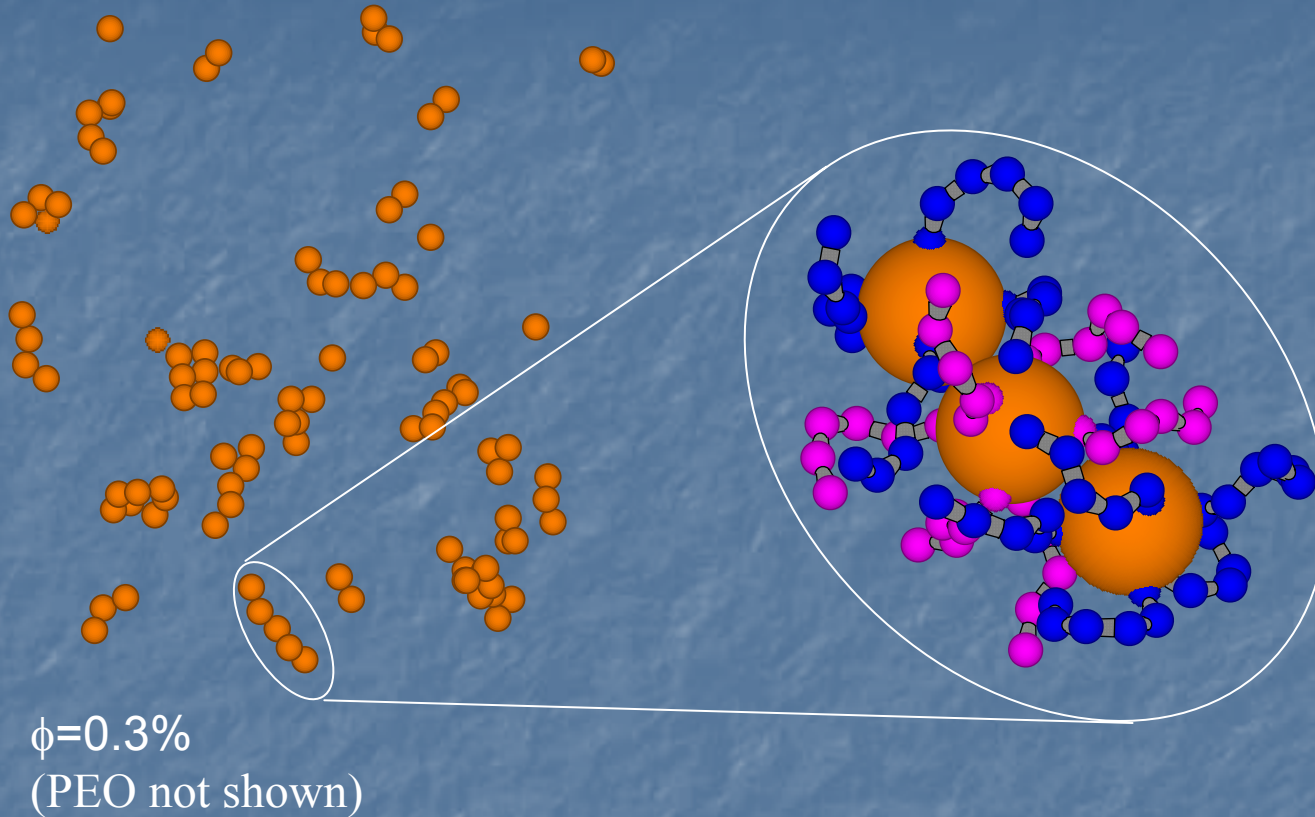


Nanoparticle Self-association

➤ Conversely, neutron scattering can play a critical role in confirming predictions of molecular simulations

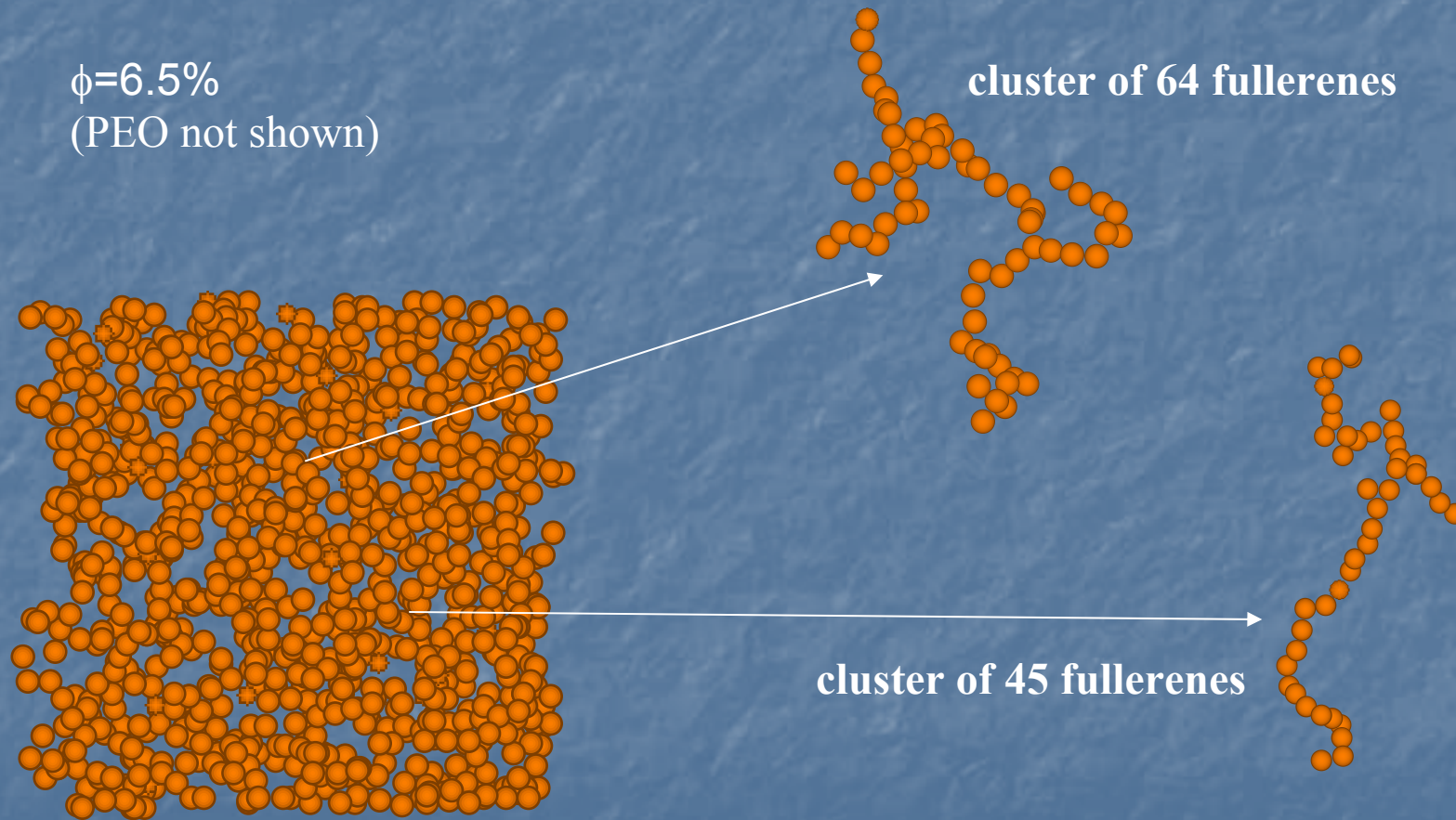


Nanoparticle Self-association



➤ Simulations show that PEO-modified fullerenes neither phase separate nor disperse in water, but rather form chain-like aggregates (6 chains)

Nanoparticle Self-association



Conclusions

- The synergism between static and dynamic neutron scattering and molecular simulations in providing important insight into nanoscale phenomena has been clearly established for polymers
 - Interpretation of experimental observations
 - Validation of simulations
 - Mechanistic insight not accessible by either technique alone
- Similar collaborative efforts will be key to unraveling the behavior of polymer-nanoparticle composites and the self-association of polymer-modified nanoparticles, including the interaction of these materials with biological structures